

# IMPROVEMENT IN BOND STRENGTH OF METAL SPRAYED COATINGS

*by*

ANIL KUMAR GUPTA

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DEPARTMENT OF METALLURGICAL ENGINEERING

**INDIAN INSTITUTE OF TECHNOLOGY KANPUR**

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# **IMPROVEMENT IN BOND STRENGTH OF METAL SPRAYED COATINGS**

*A Thesis Submitted  
in Partial Fulfilment of the Requirements  
for the Degree of  
**MASTER OF TECHNOLOGY***

*by*  
**ANIL KUMAR GUPTA**

*to the*  
**DEPARTMENT OF METALLURGICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR**  
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*Dedicated to*

*my*

*Beloved Parents*

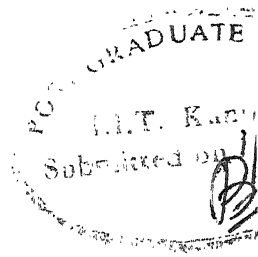
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Last but not least, I sincerely thank to all my friends who lended a helping hand in time.

A.K. GUPTA



## CERTIFICATE

It is certified that work contained in this thesis entitled "Improvement in Bond Strength of Metal Sprayed Coatings" by Mr. Anil Kumar Gupta has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

( Dr. RAJ NARAYAN )  
Professor

Department of Metallurgical Engineering  
I.I.T. KANPUR.

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## ABSTRACT

Al-Cu composite powder was prepared by coating Copper onto Al Powder by a chemical reduction process, known as electroless plating. The Copper coated Al powder was oxidised to convert Cu into CuO. This Al-CuO coated composite powder was filled in the aluminium tube and swaged to form 1/8" diameter of wire suitable for flame spraying. Similar, wires were also prepared by mixing Aluminium with Cupric Oxide powder in different proportions. During the swaging process fracture occurred. The probable causes of the fracture is investigated.

The probable reasons for this being excessive reduction in diameter in a single step, work hardening during swaging and Copper diffusion into Aluminium casing during annealing.

## INTRODUCTION

Thermal spraying processes have been developed for combating wear and providing corrosion resistance. They have been used successfully in reclamation of wornout and mismatched components. The metal spraying is being used for saving large amount of money by increasing the life of the component. It is, however, surprising that it has not gained much popularity in India.

In almost all cases of engineering application of the metal spraying the success depends upon good bond strength between the base and sprayed metal. The bond strength could be improved by proper cleaning and preparing the base material surface, by rough threading or grit blasting. However, in most cases this improvement may not be adequate.

Spraying a thin layer of molybdenum before spraying the desired metal has been found to improve bond strength. But it is a costly metal and it oxidises at around 300 °C, which may weakens and eventually destroy its bond. Therefore attempts have been made to develop alternative bond materials. Good bond strength depends upon the reactions occurring between the bond coat material and the substrate. Composite powders have been developed for enhancing the reaction and thereby improve the bond strength.

In the present investigation attempts were made to develop Al/CuO composite powder. In this procedure includes firstly, the Al powder is coated with copper by reducing Cu salt chemically and later the powder is oxidized at 400 °C for about 4-5 hrs in open atmosphere.

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Copper coated on the aluminium powder form the outer shell of the powder. In deposition such structure ensures maximum utilisation of the thermal effect of the reactions between its components.

The wire is prepared by packing the oxidised powder in a aluminium tube and swaging it afterwards. Wires were also prepared by mixing the aluminium & CuO powders in different proportions.

This investigation deals with the increasing the bond strength between a coating and substrate by increasing the temperature between the substrate and particle after impact and solidification time of particle. This can be achieved by using the material composite which produces high energy during reaction. A lot of combination of materials are available but a combination of CuO and Al are chosen for the proposed work.

## CHAPTER-2

### LITERATURE REVIEW

#### 2.1 INTRODUCTION

Flame spraying was invented in 1909<sup>(1)</sup>. The process consists of melting the material to be sprayed and projecting the molten particles to the substrate simultaneously. Various flame spraying processes differ in the method of supplying the necessary heat and the propellant used (Table 1).

The apparatus used for metal spraying consists of a gun with inlets for oxygen, fuel gases and compressed air. The raw material is fed automatically, generally in the form of wire. Other non-drawable materials are encapsulated in a flexible casing (plastic or aluminium). The necessary heat is obtained from fuel gas flame, electric arc or plasma.

##### 2.1.2 GENERAL CHARACTERISTICS OF OXY-ACETYLENE METAL SPRAYING

General characteristics of oxy-acetylene flame spraying<sup>(3)</sup> are as follows:

- (a) It is a very flexible process and can be used for any metal or alloy obtainable in the form of wire or powder to spray any other metal or alloy.
- (b) Thick coatings can be deposited easily

- (c) There is no limitations for the size of article to be coated.
- (d) Even though deposits are applied in a molten state, the base material undergoes only a small rise in temperature.
- (e) Since the base metal is subjected to only a small rise in temperature, the process does not cause any distortion, embrittlement or loss of strength in the base metal.
- (f) The metal spraying coating have microporosity. This has an advantage of retaining oil, which drastically reduce component wear in sliding.
- (g) By metal spraying it is possible to deposit a coating which has higher hardness and better corrosion and wear resistance, than the base material. Thus the sprayed component could outlast the original component.
- (h) High deposition rates can be achieved.
- (i) Spraying can be mechanised.
- (j) Relatively portable and has lower first cost.
- (k) Coating deposited by this method has porosity which restricts the use of this method for the corrosion resistance application without proper sealing.

- (l) Higher oxide content occurs when spraying is done in air.
- (w) It has poor bond strength as compared to diffusion coating, ion implantation, etc.

### 2.1.3 APPLICATIONS OF METAL SPRAYING:

The thermally sprayed coatings have wide applications some of these are listed below:

#### (a) Anti Corrosive Applications -

Coatings of pure zinc and aluminium have been widely used to protect steel components from corrosion. Typical applications being, Rail and Road bridges, Window frames, Gates, Railings Fire escapes, etc.

(b) Moulds, dies, jigs, precision patterns, electrodes etc. can be produced by this method very accurately.

#### (c) Electrical Applications -

A metal sprayed deposit can conduct electricity with an effectiveness of 50-70%. The spraying is widely used in the manufacture of capacitors and resistors to provide a conductive surface.



(d) Engineering Applications -

It can be used in industries for saving large amounts of money and providing the required surface properties easily:

- (i) Reclamation of Worn, Forged and Cast components is possible by coating the critical surfaces.
- (ii) New Surfacing of Castings and Forgings - This enables an inexpensive base material to have a surface resistance to wear, abrasion, heat or corrosion. Clutch shafts, Textile rolls, Crank shafts, Piston rods, Wheel hubs, Propeller shafts, Stern tubes, Hydraulic rams, Pump shafts, Electric motors, Paper rolls, Flanges, Rotors and Spindles etc. are the typical examples.

So, thermal spraying processes have been widely used as reliable means for combating wear by coating critical surfaces with an anti-wear, tribological or corrosion resistant coating. With increasing requirement for higher rates of production and efficiency, coatings have become an important factor in component design. Service experience have proved that component life can be increased even more than five times, utilizing proper spraying

(4)  
process .

## 2.2 BOND STRENGTH OF METAL SPRAYED COATINGS:

The aim of any coating process is that the resultant workpiece function as one component with superior properties against the environment for which it is designed. A coated material fails when the surface layer exposed to the environment separates completely or partially from the base material. This can be due to either poor contact between the substrate and the coating, or in service breakdown arising from a coating environment reaction. Therefore, the success of metal sprayed coatings depends upon good bonding strength between the base and sprayed metal.

(5)

### 2.2.1 FACTORS AFFECTING BOND STRENGTH :

The mechanisms which affects the bond strength are -

(a) Mechanical Interlocking - In this mechanism the substrate and sprayed particles are held together mechanically. So, mechanical interlocking requires rough and clean surface of substrate.

(b) Adhesion and Absorption - These two mechanism implies that the substrate and sprayed particles held together by sticking to each other. When the part of the substrate gets molten giving

rise to a boundary layer of an inter-metallic compound. Which and  
 this bridges and links the substrate to the sprayed material (6).  
 This phenomenon occurs favourably when temperature is high,  
 sprayed particles are small and impact contact area of the  
 substrate with coating material is high (7).

(c) Surface Energy - High surface energy results wetting of the  
 surface (8). The surface energy is proportional to the melting  
 point of the metal.

(d) Diffusion - Sprayed materials may be subsequently heated at  
 730 to 1090 °C to provide a dense, uniform coating, metallurgically  
 bonded to base material. At these temperatures, the coating melts,  
 coalesces, homogenizes, and begins to diffuse into the base metal  
 to form an interfacial alloy layer. The thickness and hardness of  
 this layer vary with time and temperature of diffusion and with  
 composition of the sprayed coating (25).

### 2.3 TECHNIQUES OF IMPROVING BOND STRENGTH:

Some of the above mechanisms can be influenced for  
 improving the bond strength by following methods:

### 2.3.1 SURFACE PREPARATION

Surface preparation is required to improve the mechanical interlocking of the sprayed particles with the substrate. The steps of surface preparation are as follows:

(a) Surface Washing - The surface washing is required to remove any grease or dirt present on the surface. Table 2 outlines broadly the type of surfaces and various macro-cleaning/Treating

(2)  
procedures adoptable .

(b) Roughening - It has been reported (9) that by increasing the surface roughness, bond strength increases significantly. The roughening of the surface provides an effective base for interlocking with particles. Roughness can be increased by -

(i) Grit Blasting - In this process, the angular chilled iron grits are used on the surface to be coated. The grit-size ranges from 14-100. The action of abrasive blasting increases the surface area of the workpiece significantly. Grit type and condition are important for improving the roughness of the substrate. Blasting speed and nozzle-substrate distance have no effect on surface

(10)  
roughness .

(ii) Machining - It is not feasible to grit blast the cylindrical surface. Therefore, V threads approximately 0.5 mm pitch are machined on the surface to be coated.

(c) Bond Coats - Some materials to be coated may be too hard to roughen adequately by grit blasting. To avoid the risk that a coating not adhere properly under these circumstances, a preliminary thin layer of a bond coat is applied. This thin layer can serve as an anchor for material to be sprayed on top of it.

Mo is used as a bond coat because it can adhere strongly to clean and smooth surface and provide a secondary rough surface for the metal to be sprayed. It is reported that for most plasma sprayed coatings the bond strength can be improved by using Mo as bonding material<sup>(11)</sup>.

### 2.3.2 COATING THICKNESS:

The max. thickness of given coating is often limited by the increase in residual stress with coating thickness. Residual stress in a coating changes the apparent bond strength<sup>(12)</sup>. The internal stresses are developed due to mismatch of coefficient of thermal expansion. This happens particularly for low melting point materials. The internal stresses are also developed due to mounds or depressions created by compressive or tensile stresses when cooled to the room temperature<sup>(13)</sup>.

### 2.3.3 PREHEATING:-

Preheating should be accomplished as rapidly as possible to minimise distortion and oxidation. A slightly reducing flame

may be used, but heating by reduction is preferred when the size of the parts permits to its use.

Typical preheating temperature are from 150 to 320 °C. Occuluded moisture can be prevented by preheating the surface to 35 °C. Preheating at 260 to 370 °C results in a more favourable stress distribution in the finished coating, and improves the bond strength by providing greater particle deformation and increased oxide cementation (25).

#### 2.3.4. SPRAYING DISTANCE:

The distance between the tip of nozzle and substrate should vary between 4" to 10 for good bond strength (3). The spraying distance affect the different parameters in the given ways:

##### (a) Particle Temperature

When the particle hits on the substrate, the temperature should be high enough to cause diffusion in the substrate. Due to diffusion the bond strength increases. The spraying distance controlls the temperature of the particle when it hits on the substrate. Larger the spraying distance more the heat loss due to convection and radiation to the surroundings and less will be the bond strength and vice-versa (15).

## (b) Velocity of the Particle

In the thermal spraying process the bonding between the substrate and coating particles is predominantly due to mechanical interlocking. Therefore, higher velocity or pressure of impact of the particle on substrate results good mechanical interlocking, which induces good bond strength. The larger the spraying distance greater the loss of kinetic energy of the particle due to air resistance, and this results inferior bond strength (15).

### 2.3.5 ANGLE OF DEPOSITION

Thermal spraying process is a line of sight process in which the structure of the, coating is a function of the angle of deposition. Normally coatings with the higher density and bond strength are achieved at 90° angle of deposition. This limitation may cause problems in coating of complex parts, particularly those with narrow grooves and sharp angles (16).

### 2.3.6. USING EXOTHERMIC MATERIALS

It has been reported (16) that a self bonding material which is a combination of Cu and Al, when sprayed produces self bonding coating of copper aluminide by an exothermic reaction. It is also reported (5) that the reaction enthalpy produced after the reaction between CuO and Al is 1212kJ/mol. This contributory heat

of reaction makes the particle hotter rather than cooler as it strikes on the substrate. In fact, this exothermic reaction, continues for few micro-seconds after the particle strikes the base material, causing an alloying of the materials and form a metallurgical bond. This produces a dense coating.

(16)

It is reported that mixing of aluminium with Cu, in any proportion in the powder form, does not cause an exothermic reaction with bonding to base. It is also that the optimum exothermic reaction of Cu and Al is produced during spraying provided that the materials are in controlled proportions and in an intimate contact. Using the electroless coating method the Al can be coated by Cu in such a way that Al is inner core and Cu as outer shell.

Since the Cu outershell diminishes the oxidation of Al during spraying. The relative amount of metal participating in the reaction grows. Which enables coating layers to melt more intensively. Otherwise, the oxidation of Al core during deposition is found to proceed very vigorously with the formation of  $\text{Al}_2\text{O}_3$ . When the temperature of the powder reaches to

approximately  $650^\circ\text{C}$ , the Al and Cu react and evolve a great amount of heat. Table No. enlists the reaction enthalpy of aluminium with some selected metal oxides.



## 2.4 ELECTROLESS COATING

Electroless plating is also known as autocatalytic plating or chemical plating. These plating are based on the process of catalytic reduction of metal salts. The commonly used reducing agents are Sodium hypophosphite, formaldehyde, sodium amino beranes. The electroless baths are so formulated that the metal salt and the reducer will react only in the presence of a catalyst.

In order to build up a thickness, the deposited metal has to be a catalyst for the reaction. Also, for the reaction to start the base material has to be either catalytic or has to be activated by the application of a catalyst on the substrate. This technique is important when non-conductors (like plastics) are metallized. The commonly used activators are compounds of precious metals, like gold, platinum or palladium (20).

### 2.4.1 GENERAL PROPERTIES:

The cost of electroless plating of a component is higher than that of conventional electro-plating, due to use of more expensive chemicals and necessity of careful analytical control of the bath required. As no external current is employed a uniform coating thickness will result. General properties of can electroless coating are as follows:

- (i) Uniform coating thickness
- (ii) Good throwing power
- (iii) Coating is harder than electro-deposition metal as other element(e.g.phosphorous)are incorporated in the structure.
- (iv) The deposit can be further hardened by heat treatment at  
 $400^{\circ}\text{C}$  for 1 hr.
- (v) The deposit has good wear resistance
- (vi) Very low ductility (1-3% elongation)
- (vii) Low porosity leads to good corrosion resistance
- (viii) Solutions are expensive
- (ix) Slow rate of deposition
- (x) Careful control of the bath required.

## 2.5. TESTING OF COATINGS

### Objectives -

Objectives <sup>(21)</sup> of adherence testing generally are one or more of the following:

1. Ascertain if adherence is adequate for a projected service.
2. Assess the effects of changes in processing conditions
3. Rank coating-substrate systems according to the adherence values measured for each
4. Obtain fundamental knowledge and understanding of adherence mechanisms

5. Gain fundamental insights into mechanisms by which coating-substrate systems undergo adhesive and/or cohesive failure.

#### 2.5.1 METHODS

A wide range of schemes for mechanical testing of coating-substrate adherence was reviewed<sup>(21)</sup>. The treatment here is restricted to methods that might reasonably be considered for testing coatings applied by some thermal spray process. There are eleven categories of testing methods, which are listed below:

- (i) Early strain methods
- (ii) Direct, tensile pull-off method
- (iii) Modified ollard test
- (iv) Topple or moment methods
- (v) Lap shear method
- (vi) Napkin ring test
- (vii) Rod and ring test
- (viii) Double cantilever beam method
- (ix) Double Torsion test
- (x) Four-point flexure test
- (xi) Impact separation methods.

Each method has got some advantages over other. But due to simplicity in carrying the test, Direct Tensile Pull-off Method for Testing the Coating is proposed for the present investigation.

### 2.5.2 DIRECT TENSILE PULL-OFF TEST

In the direct tensile pull-off test<sup>2,20,21,32</sup> an adhesive (typically an epoxy or cyanoacrylate is used to stick the bare flat end of a metallic pull rod to the exposed surface of the coating to be tested. A second pull rod is attached in similar fashion to the backside of the substrate. Originally, a jig is used to hold the pull rods and specimen in proper alignment till the adhesive cures. A uniaxial tension sufficient to separate the coating from its substrate is then applied. The coating bond strength is taken as the ratio of  $F/A$ , where

$F$  is the tensile force required to remove the coating and  $A$  is the nominal area over which failure occurs.:

### 2.5.3 PROBLEMS AND PRECAUTIONS

- (i) Proper alignment is a critical issue. Bending moments which cause non-uniform loading of the coating-substrate system<sup>33</sup> can result in substantial errors .
- (ii) If the coating is porous then the adhesive can impregnate sufficiently into the coating of the substrate which can give a false result in the measurement of bond strength.
- (iii) Values obtained from tensile pull-off test for the adherence also depend upon the thickness of the adhesive film and its rheology<sup>16,17,21</sup> .

- (iv) Residual stresses can be set up in the coating substrate system prior to testing as a consequence of coefficient of thermal expansion mismatches between this coating and substrate. And the mode of attachment of the pull rod to exposed coating surface.
- (v) Another difficulty that pertains to the direct, tensile pull-off method, as well as to several others, stems from the fact that externally generated vibration, often random, transmitted into specimen at the time of testing; can affect the result adversely. The problem can be overcome by isolating the specimen during testing, using proper material and designs that absorb and/or deflect the vibration. Loading character and distribution.

The standard method of tensile pull-off test uses a coated rod of 40mm face diameter. The rod was then glued to another rod and the bond strength was determined from the stress at which the two rods could be pulled apart.

## CHAPTER-3

### EXPERIMENTAL PROCEDURES

#### 3.1. Preparation of Cu Coated Al Powder:

##### 3.1.1 Pretreatment of Al Powder:

Since it was not possible to Cu-coat as received Al powder it was necessary to pretreat it several pretreatment solutions and procedures are described in literature<sup>17,18</sup>. The following pretreatment procedure was found to give good results:

##### (a) Alkali Treatment

For degreasing the powder, 200 cc of tap water was taken in a 500 ml beaker. Approximately 5 gms. of -325 meshed aluminium powder was slowly added to it. To this 10 cc. of 1% Sodium hydroxide (NaOH) solution was added. With stirring for 3-4 minutes, Aluminium powder was allowed to settle.

##### (b) Rinsing

Alkali solution was decanted and the powder was washed 2-3 times with tap water, in order to remove the traces of alkali, leaving about 200 cc of water after final rinsing.

### (c) Acid Treatment

5 cc of 5% sulfuric acid ( $H_2SO_4$ ) and 2 cc of 1% Hydrofluoric Acid (HF) were added slowly to the above with stirring. Acid was decanted after 2-3 minutes.

### (d) Washing

The powder was washed thoroughly 2-3 times with tap water to remove the acid completely. Final washing was done with distilled water.

### (e) Drying

The powder obtained after filtration was air dried in an oven at  $80^\circ C$  for 4 to 5 hours. This resulted in slight agglomerated mass which was grounded using glass pestle. This was stored in air tight container for subsequent plating.

The above process were repeated for the Treatment of the adequate quantity of the powder required for electroless coating and subsequent wire formation.

(19)

### 3.1.2 Preparation of bath for electroless Cu Coating

The electroless Cu plating bath (Table III) was prepared by first dissolving  $CuSO_4 \cdot 5H_2O$  with Rochelle Salt in water. To this NaOH in the form of a solution was added.

This gave a deep blue colour solution. If the above sequence was not followed, the bath decomposed instantaneously and a precipitate was formed. Formaldehyde was added at the last moment when the coating was started.

### 3.1.3 Cu Coating of Al Powder

500 ml of the above bath was used for coating 4 gms. of pretreated Al powder, while coating was in progress contents were thoroughly stirred. After 15 minutes, when the coating was over, which was assured by the change of colour of the bath from deep blue to bluish brown and also the ceasing bubbles, it was allowed to settle for 15 minutes and decanted. After washing with water first and acetone next, the coated powder was stored in vacuum desiccator.

If 400 ml of the bath was used for coating 4 gms of Al powder following the above procedure. This resulted in Al + 23.34% Cu composite powder.

The above process is repeated for the required amount of powder to be coated.

### 3.2. Determination of Cu % in Al-Cu Composite Powder

1 g of the coated powder was mixed with 30 ml 50%  $\text{HNO}_3$  solution which dissolved Cu, leaving Al powder. This was filtered through G-4 crucible and dried at 150°C. The loss in weight of the sample gave the amount of Cu in the composite powder.



$$\% \text{ of Cu} = [ 1 - \text{wt of Al} ] \times 100$$

Average of 3 sample was taken as the %Cu (Table IV) gives the composition of powders prepared.

### 3.3 Oxidation of the Cu layer in the composite powder

About 95% of CuO can be obtained in the presence of  $\text{p}_{\text{O}_2}$   
 = 1 atom and at 400°C.

4 gms of Cu coated Al composite powder was taken in a Test Tube and was hanged this tube with the help of a wire in the furnace and heating the furnace gradually to 400°C and was maintained this teep for 4 to 5 hours. A dark blue colour of powder was observed which indicates the formation of ground 500A thickness of CuO. This thickness is comparable with the coating of Cu on Al powder.

The same process is repeated for whole amount of Cu coated Al composite powder.

### 3.4 Preparation of Al and CuO Mixed Powders

- 325 mesh size powder of Al and CuO taken in required proportion in a mortar and mixed by using a pestle for around 2 hrs. This proportion is comparable to the Cu coated Al powder and their oxidised. The compositions of various proportion are shown in Table VI.

### 3.5 Preparation Wire using Al-CuO composite powder:

In a cylindrical tube of length 12.5 cm and outer diameter 0.5" (1.25 cm), inner dia 0.95 cm which was closed at one end. Al-CuO powder are filled from the other end. The powder was then rammed using a glass rod manually. The open end of the tube was closed. The so filled tube was used to make the wire of dia. 1/8" (0.317 cm) suitable for flame spraying gun. This was done by successive operations of swaging and annealing at about <sup>o</sup>360 C for 10 minutes.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 RESULTS

##### 4.1.1 Electroless Coating of Cu on Aluminium Powder -

As shown in Fig.1 the uncoated aluminium powders are irregular in shape. One cycle coated powders are more regular in shape as compared to uncoated powder as shown in Fig.2.

The average coating thickness of copper in Al-CuO coated composite powder is  $1.511\mu\text{m}$  in one cycle coating (Fig.3). The average weight percentage of copper achieved in Al-Cu composite powder is 26.34%.

##### 4.1.2 Swaging of Encapsulated Aluminium Tube Using Al-CuO Powder-

Cu coated aluminium powder encapsulated into a aluminium tube was in the first stage, given a 30% reduction by 3 steps of swaging. This was followed by annealing at  $360^{\circ}\text{C}$  (annealing temperature of aluminium) for 10 minutes. This annealed wire was then given a second stage swaging of around 20% reduction in one step. However, the wire failed due to cracking (Fig.4)

Another wire sample of Cu coated Al powder was encapsulated in another Aluminium tube was given the above deformations by swaging but without intermediate annealing, this wire also failed in the second stage of swaging (Fig.5)

Mixture of Cu and Al was encapsulated in the required composition again. Swaging is performed, with and without annealing but failure occurred after same reduction.

#### 4.1.3 Fractographic Investigation of the Fractured Surface -

Fractography of the fractured surface is shown for both, with and without annealing of fractured wire after swaging. Fractography of the fractured surface shows the cleavage fracture combined with the plastic deformation for annealed wire (Fig.6). And fractography of the fractured surface shows failure due to excessive work hardening in case of without annealed wire (Fig.7).

## 4.2 DISCUSSION

During the swaging of the powder filled Aluminium tube the swaging would be smoother with the more number of dies used or more number of steps performed. So, when the swaging is performed in more number of steps, the amount of pulsative load will be distributed in steps, for a particular amount of overall reduction to be performed. As a results, the amount of load per steps of swaging will be less and load applied is also uniform across the circumference of the tube. Therefore, chances of failure of the tube is less and vice-versa.

Ideally, the 1/2" diameter rod or tube would be swaged to 1/8" diameter of rod/tube in 8 steps. Approximate reduction in each step being around 10%. However, dies used in step 4,6,7 were

missing and reduction had to be given in 5 steps. This fracture is occurring due to missing of dies which creates a large size difference between die and tube. Which would become too small to hold the whole tube and thus induce the uniform hydrostatic stress around the circumference. Due to this effect, a part of rotating tube comes into tension and another remains in compression alternatively. As a result, this causes bulging of the tube and fracture is occurring.

The flow of metals is generally found to be very sensitive to the rate of deformation. In the swaging process impulsive force is applied at a very high rate, this produces high rate of deformation. The rapidly applied load has no time to be distributed uniformly throughout the entire cross section of the tube. This causes the remote portion of the cross section from the surface remains undisturbed, which will give the stress gradient across the cross section of tube. Therefore the stresses on the surface of tube is more. As a result, any microvoid present on the surface of the aluminium tube, may be propagated and convert into a crack which may results in a form of fracture.

The fracture analysis were performed for the annealed wire which reveals following information:

- (a) Fractography of the fractured surface of the annealed tube is shown in Fig.4.

- (b) Fractography of cross section of the swaged tube shows that a substantial amount of diffusion is taking place on the interface of Aluminium tube and copper coated Al powder filled in it (Fig.8)
- (c) The microhardness of Aluminium tube across the thickness of tube after fracture reveals that the hardness at the outer circumference is lower than at the interface of powder and Aluminium tube. The hardness distribution across the thickness of the tube is shown in Fig. 10.
- (d) Fractography of the fracture surface across the thickness shows the river like pattern with fibrous structure(Fig.6).

The aluminium tube with annealing becomes soft but side by side the diffusion of Cu is also taking place at the interface of the tube and powder. It is reported that Cu acts as the strengthening second phase materials the aluminium<sup>23</sup>. And it is also reported that the material strength have pronounced effect on the fracture toughness of a given material, in general strength increases, fracture toughness decreases<sup>24</sup>.

Due to atomic matching or coherency between the lattice of the precipitate (Cu) and aluminium matrix the formation of a coherent precipitate in a precipitation hardening system occurs in Al-Cu systems. After cooling from solid solutions the alloy might contains regions of solute segregation or clustering. The clustering produces local strain. As a result, hardness of that

(23 )  
zone is higher .

(24 )

Detailed experiments demonstrate that the segregation of a layer of a few atoms thick of some element or compound is sufficient to cause embrittlement. This causes cleavage type of fracture when subjected to impulsive loading during the swaging process. Fractography of the (Fig.6) fractured surface also shows the riverine structure which confirms the cleavage type of fracture. But these fracture surface also shows fibrous structure, which demonstrate that some amount of deformation also occurred. So, this fracture is occurring due to cleavage phenomenon.

The fracture analysis for the swage wire without annealing were also performed, which reveals the following information:

- (a) Fractography of the fractured surface of the tube is shown in Fig.5.
- (b) The fractography of the cross section of the swaged tube, shows the clean interface between the tube and powder. It does not show any diffusion of copper in the aluminium (Fig.9).
- (c) The microhardness of the aluminium tube across the thickness of the tube reveals that the hardness is higher at the outer circumference of the tube than at the interface of powder and tube. The hardness distribution is shown in Fig.11.

## CHAPTER 5

## CONCLUSION

Following conclusion can be drawn on the basis of present investigation:

- (a) Electroless plating method is quite suitable for coating copper on aluminium powder. In a single coating cycle the weight percentage of copper in the composite powder, was about 26.34% in the present investigation. The average coating thickness of Cu in Cu-Al coated powder, was obtained about  $1.511\mu\text{m}$ .
- (b) Aluminium tube filled with Al-CuO composite powder and mixtures of Al-CuO powder failed during swaging. The probable reasons for this being excessive reduction in the diameter in a single step, work hardening during swaging and Copper diffusion into Aluminium casing during annealing.



## CHAPTER 6

## SCOPE FOR FUTURE WORK

1. Missing dies should be arranged, before starting the swaging process, for achieving the swaging without fracture.
2. Al-CuO coated composite powder can be encapsulated into Copper tube to avoid the hardening effect at the interface between the powder and tube, due to diffusion of copper in the tube during annealing process.
3. Possibilities of electroless plating to increase the increase the copper content in Al-CuO coated composite powder by re-coating of the coated powder may be studied.

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TABLE-I  
**METAL SPRAYING PROCESSES**

Type of Energy	Source of Energy	Atomising Gas	Material form	Environment	Process
Electrical Resistane heating	Induction heating	Argon	Molten metal in a Crucible *	Vacuum Shielding gas	Molten Metal Spraying
	Induction heating	Compressed air	Wire(a)	Normal atmosphere	In chamber
	High Voltage	Shielding gas	Wire	Shielding gas	induction spraying
		None	wire	Normal atmosphere	High voltage Flame Plating(capacitor discharge)
Electricity	Electric arc	Compressed air	Two wires	Normal atmosphere	Electric-arc spraying
	Plasma	Shielding gas	Two wires	Shielding gas	In Chamber arc spraying
		None	Powder	Normal atmosphere	Plasma powder spraying
				Shielding gas	Plasma powder spraying in a chamber
Chemical reaction	Fuel gas flame/ compressed air	None	Powder	Normal atmospher	Powder flame spraying
	Oxy-fuel gas	None	Powder	Normal atmosphere	Powder flame spraying
	Very rapid combustion	Compressed gas	Powder	Normal atmosphere	Powder flame spraying
		Compressed air	Wire	Normal atmosphere	Oxyacetylene wire Spraying
		None	Powder	Normal atmosphere	Flame plating
		Shielding gas	Powder	Normal atmosphere Shielding gas	Flame plating

\*

(a) Wire can be single or multiple, or powder cored; powder and wire can be 'fed' simultaneously.

TABLE-II  
SUBSTRATE CLEANING OPTIONS

<u>SURFACE TYPE</u>	<u>TREATMENT</u>
(i) Dust covered	Suction
(ii) Solid dirt, loosely adherent	Brush (Soft wire), & Suction
(iii) Solid dirt, firmly adherent	Abrasion or blasting with right size grit or impact treatment with sand, metal costs, glass beads or ceramic granules
(iv) Organic : grease, oil	Organic solvents wash
(v) Inorganic: Scales of known composition: Vizoust	Abrasion, suitable acid and/or alkali cleaning with intermittent washing, electro-cleaning, Cathodic or anodic.
(vi) Substrate which can be welteed	Washing with clean/or de-ionized water.
(vii) Light Scales	Acid/Alkali etch/wash
(viii) Fine particle or debris	Ultrasonic cleaning
(ix) Final degreasing step	Vapour cleaning with organic solvents, incorporating safety Precautions; solvents; Trichloroethylene, Xylene etc.

TABLE III: Bath Composition of electroless Copper Coating

Chemicals	Bath I	Bath II
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	10 g	10 g
NaOH	20 g	10 g
Rochelle Salt	-	50 g
EDTA	60 g	-
Formaldehyde(37%)	30 ml	10 ml
pH	12.5	12.5
Water	1000 ml	1000 ml

NOTE: -

(i) Bath II was used mostly.

(ii) pH was adjusted using 20% NaOH.

TABLE IV: Composition of Copper Coated Al Powder.

Sample No.	%Cu	% of Al
1.	27.76%	72.24%
2.	30.90%	69.10%
3.	20.37%	79.63%

TABLE V: Reaction Enthalpy of Aluminium with some selected Metal Oxides.

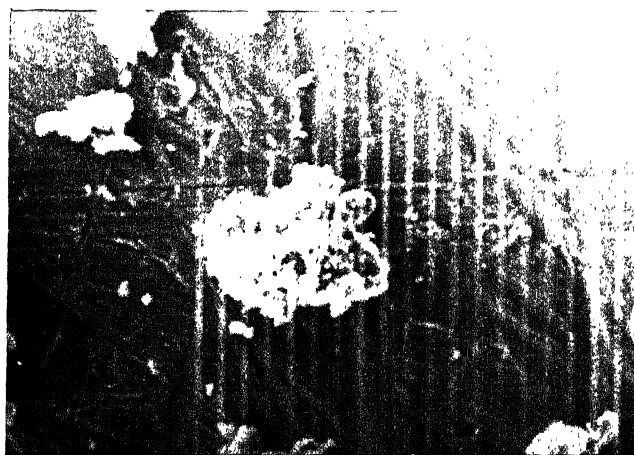
Sl.No.	Components	Reaction Enthalpy(H) kJ/mol
1.	$\text{Al} + \text{V}_2\text{O}_5$	2845
2.	$\text{Al} + \text{CuO}$	1212
3.	$\text{Al} + \text{NiO}$	919
4.	$\text{Al} + \text{WO}_3$	836
5.	$\text{Al} + \text{Cr}_2\text{O}_3$	543
6.	$\text{Al} + \text{ZrO}_2$	104

TABLE VI: Composition of Al CuO Mixed Powder

Sl.No.	Al:CuO	Products
1.	1:3.5	$\text{Al}_2\text{O}_3 + \text{Cu} + \text{Al}$
2.	1:4	$\text{Al}_2\text{O}_3 + \text{Cu} + \text{Al}$
3.	1:4.4	$\text{Al}_2\text{O}_3 + \text{Cu}$
4.	1:5	$\text{Al}_2\text{O}_3 + \text{CuO}$
5.	1:5.5	$\text{Al}_2\text{O}_3 + \text{Cu} + \text{CuO}$

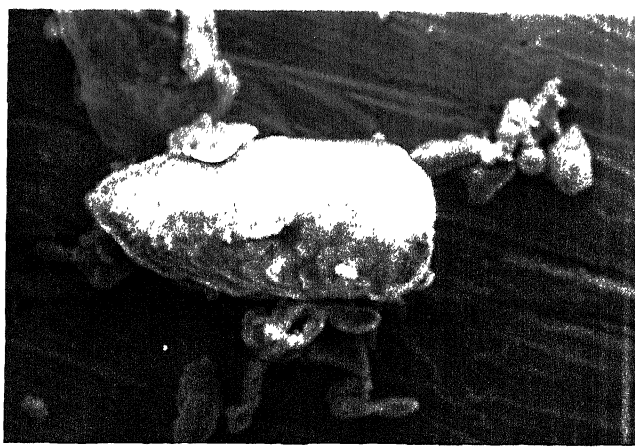
TABLE VII: Coating thickness of the Cu Coated Al Powder

S.No.	Sample No.1	Sample No.2	Sample No.3	Sample No.4	Sample No.5
1.	0.75 $\mu\text{m}$	0.75 $\mu\text{m}$	2.75 $\mu\text{m}$	0.75 $\mu\text{m}$	2.75 $\mu\text{m}$
2.	1.000 $\mu\text{m}$	1.000 $\mu\text{m}$	2.125 $\mu\text{m}$	1.000 $\mu\text{m}$	2.750 $\mu\text{m}$
3.	0.875 $\mu\text{m}$	1.000 $\mu\text{m}$	1.500 $\mu\text{m}$	1.000 $\mu\text{m}$	2.125 $\mu\text{m}$
4.	0.500 $\mu\text{m}$	1.125 $\mu\text{m}$	1.500 $\mu\text{m}$	1.125 $\mu\text{m}$	2.000 $\mu\text{m}$
5.	0.625 $\mu\text{m}$	1.500 $\mu\text{m}$	2.000 $\mu\text{m}$	1.000 $\mu\text{m}$	1.750 $\mu\text{m}$
6.	0.750 $\mu\text{m}$	1.750 $\mu\text{m}$	1.750 $\mu\text{m}$	1.250 $\mu\text{m}$	1.750 $\mu\text{m}$
7.	1.250 $\mu\text{m}$	1.500 $\mu\text{m}$	1.750 $\mu\text{m}$	1.375 $\mu\text{m}$	2.500 $\mu\text{m}$
8.	1.000 $\mu\text{m}$	1.250 $\mu\text{m}$	2.250 $\mu\text{m}$	1.500 $\mu\text{m}$	1.500 $\mu\text{m}$
9.	0.500 $\mu\text{m}$	1.500 $\mu\text{m}$	1.625 $\mu\text{m}$	1.750 $\mu\text{m}$	2.500 $\mu\text{m}$
10.	0.500 $\mu\text{m}$	1.125 $\mu\text{m}$	1.750 $\mu\text{m}$	1.500 $\mu\text{m}$	1.250 $\mu\text{m}$
Average Thickness	0.775 $\mu\text{m}$	1.264 $\mu\text{m}$	1.917 $\mu\text{m}$	1.225 $\mu\text{m}$	2.088 $\mu\text{m}$



X 1000

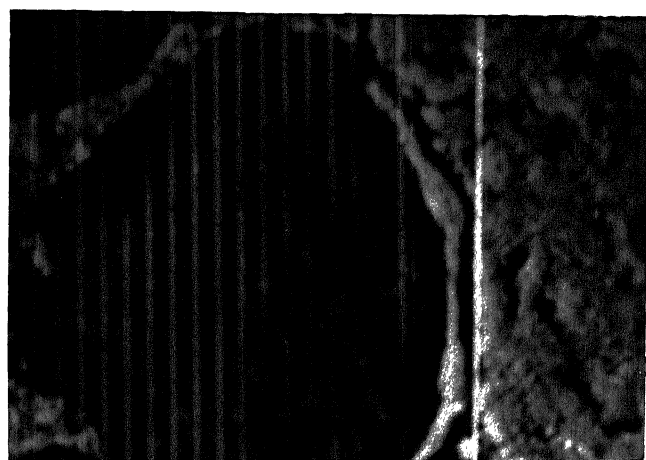
Fig.1 Scanning Electron Micrograph of the uncoated Al Powder of -325 mesh size.



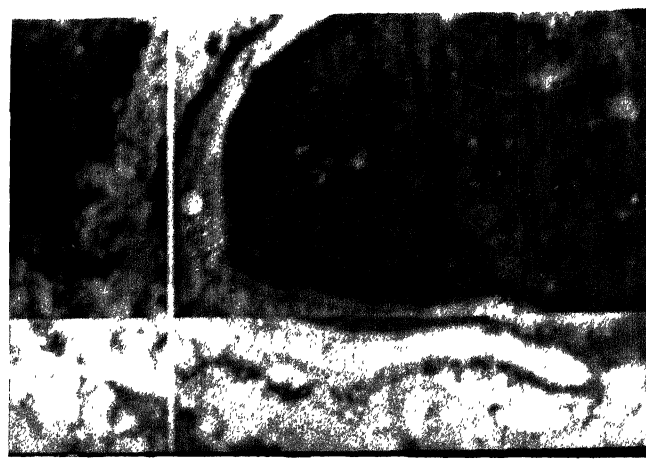
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Fig.2 Scanning Electron Micrographs of the Cu Coated Al Powder of - 325 mesh size.

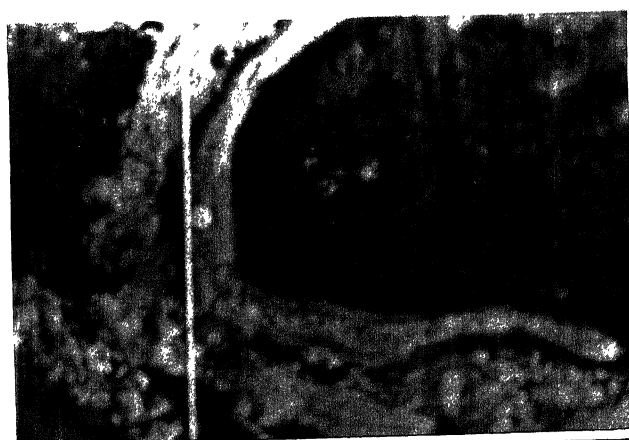




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Fig.3 Scanning Electron Micrograph of the Cross-section of Copper Coated Al Powder



X 15

Fig.4 Scanning Electron Micrograph of the Surface of CuO-Al Composite Powder filled Annealed Aluminium Tube after Fracture.



X 23

Fig.5 Scanning Electron Micrograph of the Surface of CuO-Al Composite Powder filled Annealed Aluminium Tube after Fracture.



X 160

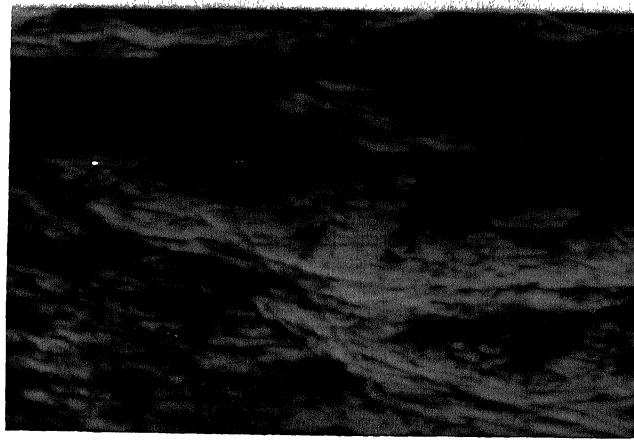


X350

Fig.6 Scanning Electron Micrograph of the Fractured Surface of the Annealed CuO-Al Composite Powder filled Al Tube.



X 2000



X 5000

Fig.7 Scanning Electron Micrographs of the Fractured Surface of the CuO-Al Composite Powder filled without Annealed Al Tube.

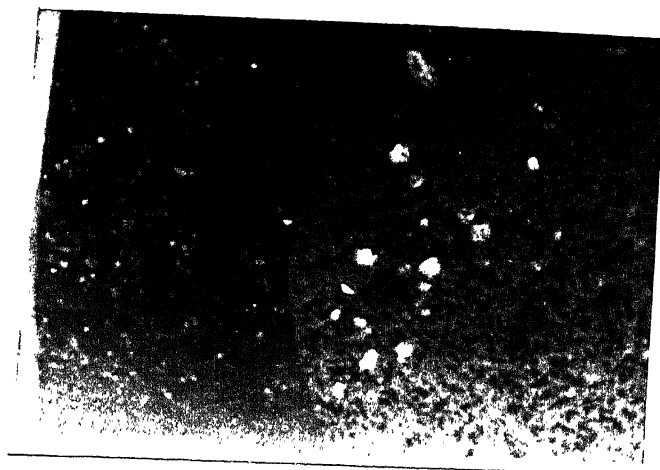


X 70



X 1000

Fig.8 Scanning Electron Micrograph of the Cross-section of failed CuO-Al filled Al Tube after Swaging with Annealing



X 60



X 1000

Fig.9 Scanning Electron Micrograph of the Cross Section of failed CuO-Al filled Al Tube after swaging without Annealing.

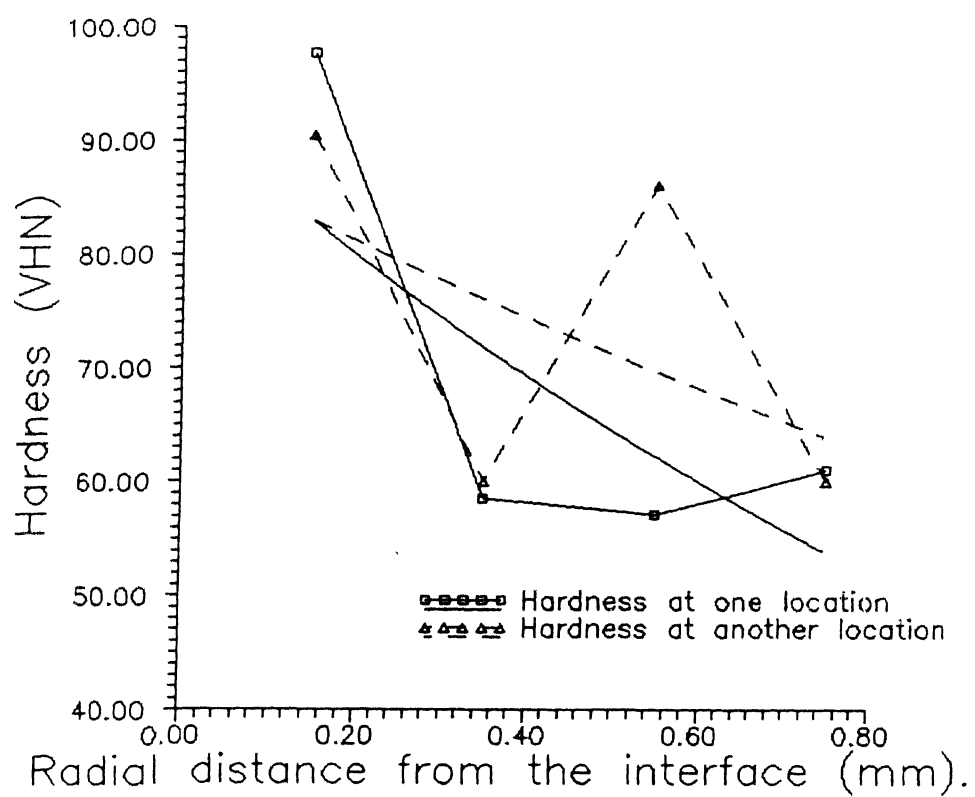


Fig.10 Hardness distribution across the thickness of the Al t (With anealing).

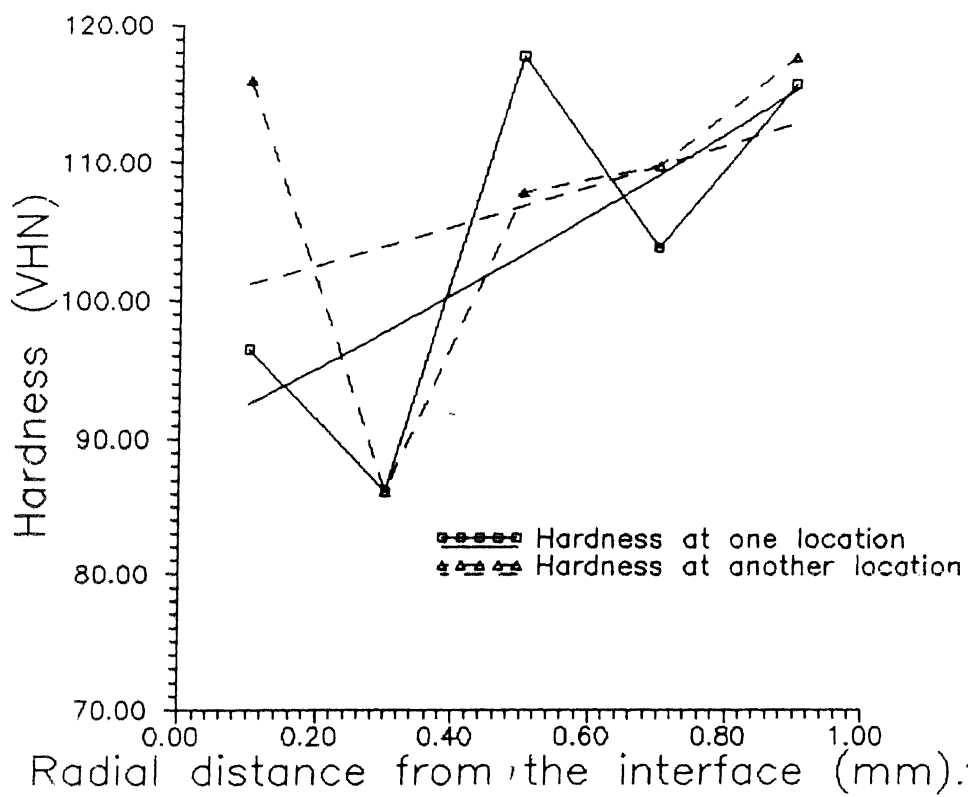


Fig.11 Hardness distribution across the thickness of the Al tube (Without annealing).



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